1-Trimethylstannylphospholes as Precursors of η5-Phospholyl Complexes. Synthesis of (η5-Phospholyl)trichlorotitanium(IV) Complexes

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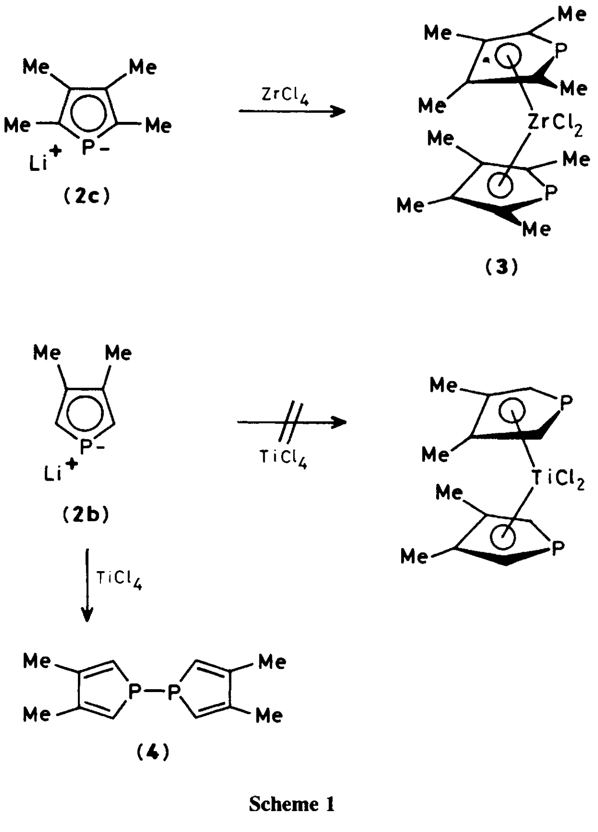
Reaction of lithium phospholides with Me_3SnCl yields 1-trimethylstannylphospholes, which in toluene–hexane solution react with $TiCl_4$, affording (η5-phospholyl)trichlorotitanium(IV) complexes.

In a recent publication,[1] we described a synthesis of the new phosphole (**1c**) together with the first *X*-ray crystal structure of a (η5-phospholyl) zirconium complex (**3**). Since only three examples of (η5-phospholyl) group 4 metal complexes were known, and in all cases with zirconium as the metal,[1,2] we wanted to know whether phospholyl complexes of the lighter group 4 element titanium could be made. The straightforward synthesis of a (η5-phospholyl) group 4 metal complex by reaction of a lithium phospholide with MCl_4, a method which was successful with zirconium as the metal,[1] failed in the case of titanium: when a tetrahydrofuran (THF) solution of lithium 3,4-dimethylphospholide is added to a solution of $TiCl_4$ in toluene, 3,4,3′,4′-tetramethylbiphospholyl (**4**)[3] can be isolated in 61% yield, Scheme 1.

This result is very likely due to monoelectronic reduction of $TiCl_4$ by the phospholide anion and subsequent coupling of the phospholyl radical thus formed. In order to overcome this drawback, we had to find another precursor of the phospholyl ligand lacking the anionic character which is probably responsible for the reduction of $TiCl_4$. We thought of using a stannyl phosphole for that purpose for the following reasons: first, covalent silyl- and stannyl-cyclopentadienes have been used as cyclopentadienylation reagents for titanium.[4] Furthermore, Abel *et al.*[5] have recently described the synthesis of an η5-arsolyl complex of manganese by reaction of a silylarsole with $BrMn(CO)_5$. Finally, a stable 1-stannylphosphole has recently been reported by our laboratory.[6]



Scheme 1

The synthesis of 1-trimethylstannylphospholes is straightforward: treatment of 1-phenylphospholes (**1**) with lithium in THF followed by $AlCl_3$[7] gives phospholide anions (**2**) which in turn react with $ClSnMe_3$, affording 1-trimethylstannylphospholes (**5**) in good (70—80%) yields.† These compounds are oils that solidify at −20°C (in the freezer) and are very air and water sensitive, Scheme 2.

When a hexane solution of these 1-stannylphospholes was added to a solution of $TiCl_4$ in toluene at 0 °C, (η5-phospholyl) trichlorotitanium(IV) complexes (**6**) were formed, and could be isolated by toluene extraction in good (65—75%) yields, as moderately air sensitive red solids which were characterized by ^{1}H, ^{13}C, and ^{31}P n.m.r. and mass spectroscopy, and elemental analysis,‡ Figure 2.

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† Satisfactory elemental analyses obtained for all new compounds. (**5a**): B.p. 120—130 °C/10 mm. N.m.r. ($[^{2}H_{12}]$cyclohexane): ^{1}H (200 MHz, p.p.m. from int. Me_4Si, *J* in Hz): 0.14 [d, $^{3}J_{PH}$ 2, $Sn(CH_3)_3$], 7.09 (dm, $^{2}J_{PH}$ 41, H_2 and H_5), 7.25 (dm, $^{3}J_{PH}$ 11, H_3 and H_4. ^{31}P-{^{1}H} (32.4 MHz, 85% H_3PO_4 ext.) −50.09. ^{13}C-{^{1}H} (50 MHz, int. Me_4Si) −7.74 [d, $^{2}J_{PC}$ 6.2, $(CH_3)_3Sn$], 134.69 (d, $^{1}J_{PC}$ 24, C_2 and C_5), 136.55 (s, C_3 and C_4). ^{119}Sn-{^{1}H}: (29.9 MHz, Me_4Sn ext., hexane) 16.42 (d, $^{1}J_{PSn}$ 532).

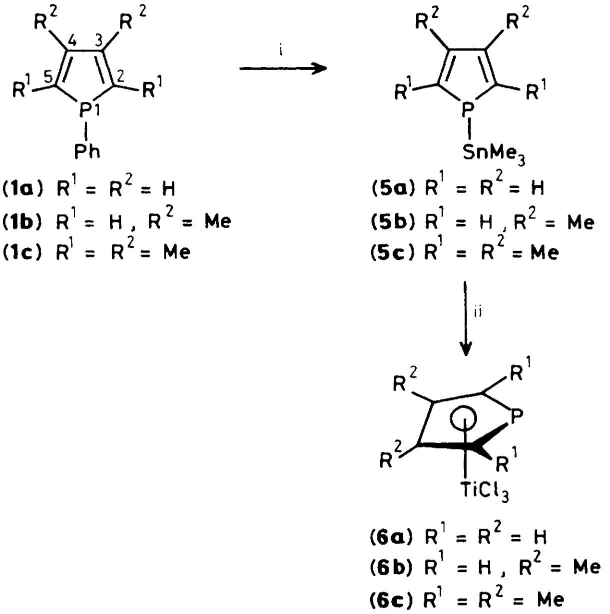
(**5b**): B.p. 60—70 °C/0.01 mm. N.m.r. (CD_2Cl_2): ^{1}H: 0.12 [d, $^{3}J_{PH}$ 2.7, $Sn(CH_3)_3$], 2.20 (s, CH_3–C_3 and CH_3–C_4), 6.55 (d, $^{2}J_{PH}$ 41, H_2 and H_5). ^{13}C-{^{1}H}: −7.41 [d, $^{2}J_{PC}$ 6.2, $Sn(CH_3)_3$], 17.51 (d, $^{3}J_{PC}$ 2.6, CH_3–C_3 and CH_4–C_4), 129.36 (d, $^{1}J_{PC}$ 19.8, C_2 and C_5), 147.70 (s, C_3 and C_4). ^{31}P-{^{1}H}: −65.09. ^{119}Sn-{^{1}H} (hexane): 23.27 (d, $^{1}J_{PSn}$ 555). Mass spectroscopy (direct inlet., 70 eV, ^{120}Sn): *m/z* 276 (M^+, 43%), 165 (100%).

(**5c**): B.p. 100—110 °C/0.01 mm. N.m.r. (CD_2Cl_2): ^{1}H: 0.15 [d, $^{2}J_{PC}$ 2, $Sn(CH_3)_3$], 2.04 (s, CH_3–C_3 and CH_3–C_4), 2.13 (d, $^{3}J_{PH}$ 10.5, CH_3–C_2 and CH_3–C_5). ^{13}C-{^{1}H}: −9.09 [d, $^{2}J_{PC}$ 5.5, $Sn(CH_3)_3$], 13.86 (d, $^{3}J_{PC}$ 2, CH_3–C_3 and CH_3–C_4), 14.24 (d, $^{2}J_{PC}$ 23.5, CH_3–C_2 and CH_3–C_5), 133.63 (d, $^{1}J_{PC}$ 14.5, C_2 and C_5), 142.39 (d, $^{3}J_{PC}$ 4, C_3 and C_4). ^{31}P{^{1}H}: −45.96. ^{119}Sn{^{1}H} (hexane): 21.20 (d, $^{1}J_{PSn}$ 577). Mass spectroscopy: *m/z* 304 (M^+, 45%) 289 (100%).

‡ Satisfactory elemental analyses obtained for all new compounds. (**6a**): M.p. 110 °C (decomp.). N.m.r. ($[^{2}H_6]$benzene, *J* in Hz): ^{1}H: 6.71 (dm, H_3 and H_4), 7.05 (dm, $^{2}J_{PH}$ 36, H_2 and H_5). ^{13}C-{^{1}H}: 134.15 (d, $^{2}J_{PC}$ 8.5, C_3 and C_4), 145.10 (d, $^{1}J_{PC}$ 62, C_2 and C_5), ^{31}P-{^{1}H}: 182.4 (tt, $^{2}J_{PH}$ 35.6, $^{3}J_{PH}$ 4.8). Mass spectroscopy (^{35}Cl, ^{48}Ti): *m/z* 236 (M^+, 100%).

(**6b**): M.p. 75 °C (decomp.). N.m.r. ($[^{2}H_6]$benzene): ^{1}H: 2.11 (s, $2CH_3$) 6.86 (d, $^{2}J_{PH}$ 35.9, H_2 and H_5). ^{13}C-{^{1}H}: 17.87 (s, $2CH_3$),144.40 (d, $^{1}J_{PC}$ 58.6, C_2 and C_5), 151.15 (d, $^{2}J_{PC}$ 8.3, C_3 and C_4). ^{31}P-{^{1}H}: 189.4. Mass spectroscopy: *m/z* 264 (M^+, 17%) 111 (100%).

(**6c**): M.p. 117 °C. N.m.r. (CD_2Cl_2): ^{1}H: 2.45 (s, CH_3–C_3 and CH_3–C_4), 2.67 (d, $^{3}J_{PH}$ 9.8, CH_3–C_2 and CH_3–C_5). ^{13}C-{^{1}H}: 16.46 (s, CH_3–C_3 and CH_3–C_4), 19.82 (d, $^{2}J_{PC}$ 22.1, CH_3–C_2 and CH_3–C_5), 51.21 (d, $^{2}J_{PC}$ 5.6, C_3 and C_4), 160.45 (d, $^{1}J_{PC}$ 54.8, C_2 and C_5). ^{31}P-{^{1}H}: 209.27. Mass spectroscopy: *m/z* 292 (M^+, 21%) 139 (100%).



Scheme 2. *Reagents and conditions*: i, Li (excess), THF, room temp., 2—3 h; $AlCl_3$ (0.33 equiv.), 0 °C, 30 min; $ClSnMe_3$ (1 equiv.), room temp., 5 min. ii, $TiCl_4$, toluene–hexane, 0 °C, 5 min.

Evidence for the η^5-phospholyl structure of compounds (**6**) comes mainly from ^{13}C n.m.r.: the resonance of carbons C_2 (and C_5) display a very high $^1J_{PC}$ coupling constant, in the 50—60 Hz range, which is typical of η^5-phospholyl complexes and phosphametallocenes including the recently described Zr complex (**3**).[1] The ^{31}P and ^{13}C signals of the ring atoms are shifted to very low field, which may be due to the strong electron-withdrawing effect of the $TiCl_3$ moiety.

In toluene–hexane as solvent, monosubstitution of $TiCl_4$ by a phospholyl group is obtained even if the 1-stannylphosphole is in excess (when $TiCl_4$ is added to a solution of the phosphole). In more polar solvents such as 1,2-dichloroethane or THF, however, the reaction seems to be more complex. A noteworthy point is finally that a good yield was obtained whatever the substitution pattern of the starting phosphole, and thus the method might be generalized to other phospholes. Our future plans include a study of the chemical properties of complexes (**6**).

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